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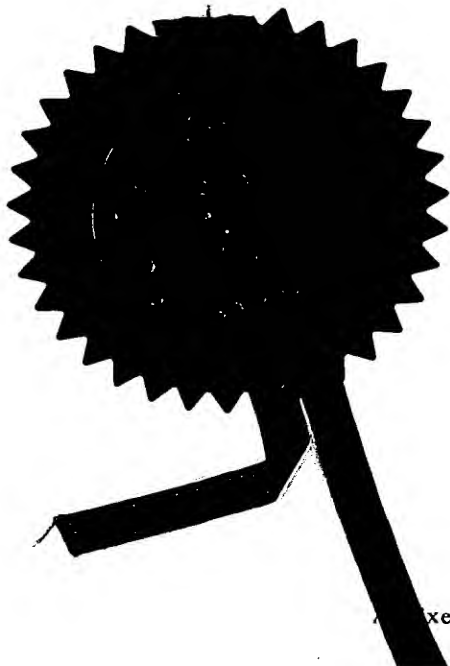
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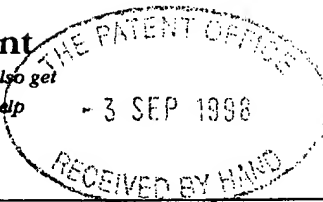
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Dated 10 September 1999

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1. Your reference

P19832GB SJC/SW

2. Patent application number

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9819228.9

3 SEP 1998

3. Full name, address and postcode of the or of each applicant (underline all surnames)

Captur Sensors & Analysers Limited
11 Moorbrook Park
Didcot OX11 7HP

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

7124605001
U.K.

4. Title of the invention

SEMICONDUCTOR GAS SENSOR
OF OZONE

5. Name of your agent (if you have one)

CARPMAELS & RANSFORD

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

43 BLOOMSBURY SQUARE
LONDON WC1A 2RA

Patents ADP number (if you know it)

83001

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Country

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Number of earlier application

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Description 8

Claim(s) 1

Abstract 0

Drawing(s) 10 *4/2*

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Statement of inventorship and right to grant of a patent (*Patents Form 7/77*)

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11. I/We request the grant of a patent on the basis of this application.

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Cayman + Runcie Date 09-09-98

12. Name and daytime telephone number of person to contact in the United Kingdom
Dr. S.J. Colgan - 0171 242-8692

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SEMICONDUCTOR GAS SENSING OF OZONE

In our previous application WO-95/35495, we described a method of measurement of ozone concentration involving the measurement of electrical resistance of a porous tungstic oxide element, held at elevated temperature (200-500°C). When the element is held at constant temperature, the sensitivity to ozone tends to vary with time and to be dependent upon the history of the device, including previous exposure to ozone. Other semiconducting oxides have been shown to exhibit resistance increases of elevated temperature in the presence of small concentrations of ozone in the air: In_2O_3 , pure and variously doped, by Takada et al, Sensors & Actuators B : Chemical 13 (1993) 404; M_0O_3 by Garlo et al., Sensors & Actuators B : Chemical 47 (1998) 92. We have now discovered that S_nO_2 also shows the effect (Figure 1), though at rather lower temperature (~200°C) and with problems of baseline stability. We believe that the phenomenon is generic to a certain general class of semiconducting oxides for which oxygen vacancies can be created at the surface, at the operating temperature, in air, in sufficient concentration to substantially affect the concentration of electronic charge carriers and hence the electrical conductivity.

We have discovered a set of methods for analysis of ozone concentration in air, which are generally applicable to the afore-mentioned class of oxides. The methods surprisingly result in (1) a significant increase in the stability of the signals generated by sensors incorporating these materials, and (2) significantly reduce the lower detection limit of the sensors for ozone to concentrations of first a few ppb, and more typically of the UV ozone analysers conventionally employed to detect this molecule. These methods involve causing a perturbation of the condition of the sensor and analysing the resulting time variation of the sensor resistance or conductance. These methods are:

(1) a perturbation of the sensor temperature, which may be small or large, in the form of a square pulse or a sinusoidal variation;

(2) a perturbation of the ozone concentration near the sensor, either by periodically switching the gas flow to the sensor through a catalyst bed which destroys any ozone present, or by simply altering the flow rate of gas over the sensor, using the hot sensor itself to cause local decomposition of the ozone present in the air.

The methods give substantially increased accuracy and stability, and consequently a greater reliability of measurement, especially at very low ozone concentration (less than 100 ppb in air). A very low detection limit for ozone can be achieved, which can be reliably sustained in measurement over a long period of time. A typical detection limit achieved using a device based on WO_3 is 2.5 ppb in air, reliably sustained without change of calibration over at least 3 months.

Method 1:

- step to a high temperature to reset the surface
- step back to a low temperature to make the measurement
- analyse the variation of resistance with time at the low temperature to obtain the ozone concentration
- repeat the sequence.

For example with a device based on WO_3 , the "high" temperature can be 400°C - 800°C and the "low" temperature can be 200°C - 500°C, with the obvious constraint that the "high" temperature should be greater than the "low" temperature.

Figure 2 shows an example. In the presence of ozone in the air, the device temperature was stepped to 600°C for 300s, then stepped back to 400°C for 300s. The time-variation of resistance at 400°C following the step back ($t=0$) is shown. The conductivity, S (reciprocal of resistance) at the low temperature shows the following variation:

$$S(t) = S_{\text{lim}} + a_1 e^{-t/\tau_1} + a_2 e^{-t/\tau_2} \quad (1)$$

where

$$S_{lim} = S_{\infty} + b_o/(O_3)$$

$$\tau_1 = b_1/(O_3)$$

$$\tau_2 = b_2/(O_3)$$

where (O_3) denotes the ozone concentration.

Here, S_{∞} , a_i are constants which depend on the time and temperature of the "high" temperature step. The b_i depend upon the temperature of the "low" temperature step, at which the measurement is made but do not depend on the high temperature step values. Typically, $b_2 \approx 10b_1$ so that the second time-dependent term is only significant at higher ozone concentration. If the measurement temperature (the "low" temperature) is decreased then the ratio b_2/b_1 increases, so again the second time-dependent term becomes less significant.

Application of method to ozone measurement

(a) by curve-fitting the data to equation (1), the values of τ_1 , τ_2 are determined. By reference to a calibration curve of τ_1 (and if necessary τ_2) against ozone concentration, the ozone concentration is obtained. The sensor and the stability of the operating circuitry are checked by checking the stability of the parameters S_{∞} , a_1 , a_2 , which are also obtained from the fit. If the measurement time is limited, or the ozone concentration is low enough, or the measurement temperature is low enough, then only one time constant will be required to describe the data, and the reliability of the parameter fit can be improved.

(b) the resistance or conductance at a particular time after the change of temperature can be determined, and the ozone concentration can be obtained from a calibration curve of this resistance against ozone concentration.

Manipulation of equation (1) shows that a linear calibration of either

conductance or resistance will be obtained if the time constants τ_1 , τ_2 are sufficiently long: i.e. at low (O_3). Figure 3 shows an example. In this example, between the calibration runs, the sensor had been used continuously, measuring ozone in urban air. It is evident that the calibration had not drifted over a period of some months. From the calibration line, a detection limit of 2.5 ppb is deduced.

Unlike (a), this method requires the parameters S_∞ , a_1 , a_2 to remain stable that is, that the surface should be fully "reset". We have found that this can be achieved by an appropriate choice of temperature and time for the "high" temperature step. For Figure 3, it was 600°C and 300s, with measurement at 400°C. Figure 4 shows the required time as a function of the temperature, for WO_3 -based devices. The higher the temperature, the shorter the time. Figure 5 shows the energy consumption during the high temperature step (power required x time required). The energy consumption decreases with increasing reset temperature. So, the higher the reset temperature the better, both for time resolution (the device is not measuring during the reset period) and for energy consumption (the less energy consumed the better for applications requiring battery power: balloon-borne instruments are an example).

(c) the time, t^* , required to achieve a particular resistance, R^* , can be measured and the ozone concentration derived from a calibration derived from a calibration curve. From equation (1), t^* varies approximately as $1/(O_3)$. The value, R^* , is chosen according to the expected ozone concentration: obviously, choosing a lower value will decrease t^* for a given (O_3). This method has the advantage of measurement simplicity: a counter is started at the end of the reset pulse and stopped when a comparator circuit senses that the measuring current through the sensor falls below a preset level.

(d) is a combination of (b) and (c). The resistance is monitored as a function of time until the end of a preset measurement time, t_m . A resistance trigger level, R^* , is also set. If, during t_m , the resistance exceeds R^* , then the

time of this occurrence, t^* , determines the ozone concentration, the sensor is reset and the sequence repeats. If, at the end of t_m , $R_m < R^*$, then the value of resistance R_m at t_m is used to determine the ozone concentration, the sensor is reset and the sequence repeats. This method gives a wide dynamic range and good response time with simple electronics.

Method 2

- oscillate the temperature by a relatively small amount e.g. $\pm 50^\circ\text{C}$
- either a square-wave oscillation between two temperatures separated by a small amount (e.g. 50°C), with a period of typically 1-10 min, or a sinusoidal oscillation with a period of typically 1-10min
- measure the phase shift (delay time) between temperature oscillation and resistance oscillation and determine ozone concentration from a calibration curve.

In this method, there will, of course, be an oscillation of resistance caused by the effect of temperature on the resistivity of the material (resistance decreases with increasing temperature). This element of the oscillating resistance will have only a small delay time (typically $\sim 0.2\text{s}$) determined by the thermal response time of the sensor. Superimposed upon this will be an additional oscillation due to the effect of ozone. The two effects can be separated using a time-gated measurement scheme. Alternatively, the device can be configured as a multi-electrode device of the type we have previously described. If such a device having two electrode spacings is arranged in a bridge circuit, then the output signal will be proportional to the ratio of the two resistances. This resistance ratio will be independent of temperature in the absence of ozone, but, because ozone is a reactive gas which shows a concentration gradient through the sensor layer, the resistance ratio will vary if ozone is present, dependent upon both time and temperature.

Now, consider the resistance oscillation due to the present of ozone, for the case of a square-wave oscillation of temperature. Equation (1) gives the

conductance as a function of time at each of the two temperatures. Because, in this method, the sensor surface is not periodically being completely preset by a step to high temperature, the parameters S_{∞} and a_j may vary with time, dependent on the history of the device and the ozone concentration. However, the parameters b_j do not so vary. Thus the time constants τ_j depend only on the temperature and on the ozone concentration. The method therefore comprises the following steps:

- (1) subtracting the instantaneous change of resistance following each temperature step
- (2) determining the amplitude of the remaining temperature oscillation, from which the ozone concentration may be determined, by reference to a calibration curve
- (3) determining the time constants for each of the two temperatures, according to equation (1), either by curve-fitting equation (1) or by calculation from the resistance values at two or more times during each period of constant temperature
- (4) deriving two further estimate of ozone concentration by reference to calibration curves for the two temperatures.

The method may be generalised to other waveforms for the temperature perturbation, e.g. sinusoidal, using the process of first filtering to remove the instantaneous resistance change caused by the change of temperature and then harmonic analysis, time-correlation function calculation or Fourier transformation to obtain the amplitudes and time constants associated with the ozone-dependent signal, then comparison with calibration curves to derive the ozone concentration.

- Method 3
- switch the air stream periodically through a suitable ozone decomposition catalyst
 - analyse the resistance variation of the sensor when the ozone is reapplied.

This method is simple to implement using switching valves.

The sensor signal when the ozone-destruction catalyst is switched out of the air stream follows equation (1). Figure 6 shows a typical response to a sequence of two pulses of ozone interspersed with ozone-free air, with the sensor at constant temperature. The increase of signal amplitude with total ozone dose is a characteristic of these devices when measured at constant temperature, as is the variation between devices. However, the time variation of the signal can be fitted to equation (1). The time constants so derived do not vary from one pulse to another, or from one device to another, wherein reasonable experimental error and the ozone concentration can be determined from the time constants, by reference to a calibration curve. As with the temperature-switching method, this method does not require the sensor resistance to stabilise in order that the ozone concentration be accurately determined.

Method 4 - periodically greatly reduce the airflow rate over the sensor, then increase it again, with the sensor at constant temperature.
 - analyse the time variation of the signal following the increase of flow rate.

This method works because ozone is decomposed within the thermal boundary layer near the sensor. The variation of signal with airflow rate normal to the sensor is shown in figure 7. At sufficiently high flow rate, the signal achieves a plateau, because ozone is transported to the surface at a rate sufficiently greater than the rate of thermal decomposition near the sensor. At lower flow rate, the signal falls reflecting the fall in ozone concentration near the sensor. At low enough flow rate, the sensor signal is virtually zero. Therefore, if the air flow to the sensor is greatly reduced, (cutting off the flow completely is, of course, one option) then the sensor resistance will relax towards the value characteristic of a zero ozone concentration. Just as in method 3, it is not necessary to attain an exact zero, however. When the flow rate is increased

again, to a value on the plateau of Figure 7, the sensor resistance will increase with time, following equation (1). Curve-fitting equation (1), or calculation from two or more points gives the time constants. By reference to a calibration curve, the time constants give the ozone concentration. The other parameters of equation (1) can be used to diagnose continued reliable operation of the sensor.

The power drawn by the sensor device will depend on the air flow rate.

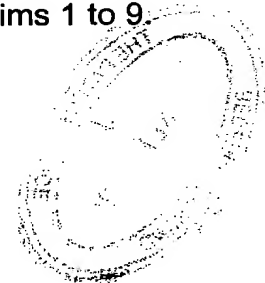
Therefore, monitoring the sensor power consumption serves two purposes:

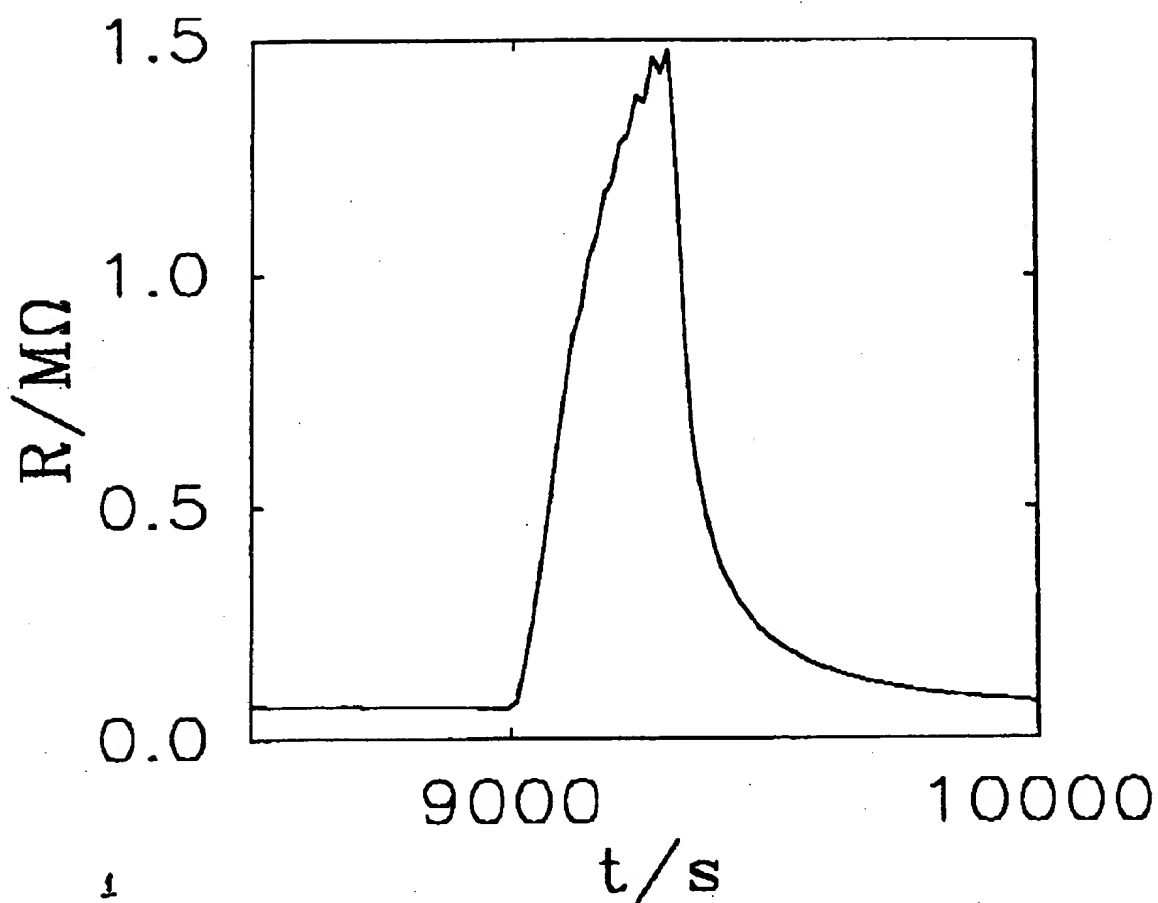
(a) it checks that the required flow rate is indeed being delivered and hence diagnoses failure of any of the other components of the system or blockage of the pipe work;

(b) it provides a trigger signal to actuate the resistance measurement circuits at the correct time, thus compensating for delays in the flow lines.

CLAIMS;-

1. A method of sensing the concentration of ozone in a gas mixture using a semiconductor gas sensor having a resistivity sensitive to ozone, which comprises perturbing the sensor operating temperature and analysing the resultant resistance of the sensor following perturbation.
2. A method according to claim 1, in which the perturbation is a square wave pulse or is sinusoidal.
3. A method according to claim 1 or 2 in which the perturbation comprises increasing the sensor temperature followed by a temperature reduction at which the resistance is analysed.
4. A method according to any preceding claim wherein the sensor resistance is analysed as a function of time.
5. A method of sensing the concentration of ozone in a gas mixture using a semiconducting gas sensor having a resistivity sensitive to ozone, which comprises perturbing the ozone concentration over the sensor and analysing the resultant resistance of the sensor following perturbation.
6. A method according to claim 5 wherein the perturbation comprises reducing the ozone concentration to zero or periodically changing the flow rate of gas over the sensor.
7. A method according to any preceding claim in which the sensor is a semiconductor oxide for which oxygen vacancies can be created at the sensor surface, at the operating temperature, in air, in sufficient concentration to affect substantially the concentration of electronic charge carriers and hence the resistivity.
8. A method according to claim 7 in which the sensor is WO_3 , In_2O_3 , or SnO_2 .
9. A method of sensing the concentration of ozone in a gas mixture according to claim 1 or 5 substantially as hereinbefore described.
10. An apparatus for conducting the method of any of claims 1 to 9.





¹
Figure 4 Response of SnO₂ device at 175°C to 50ppb O₃ in air

Figure 2 Ozone response of WO_3 device

$T_{\text{high}} = 600^\circ\text{C}$, $T_{\text{low}} = 400^\circ\text{C}$

time constants for fitted curve: $\tau_1 = 30\text{s}$, $\tau_2 = 130\text{s}$

Ozone concentration = 50 ppb

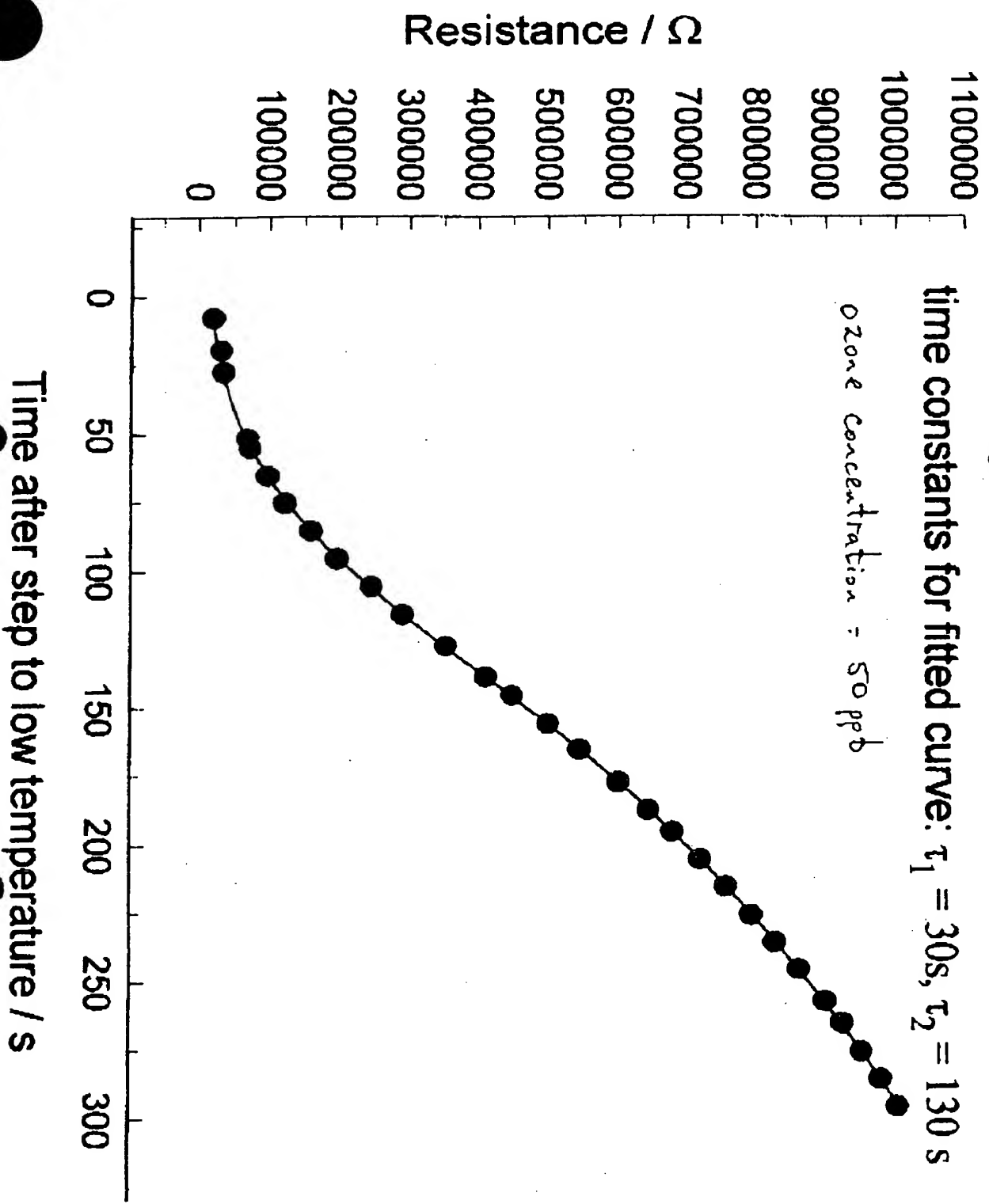


Fig. 2a

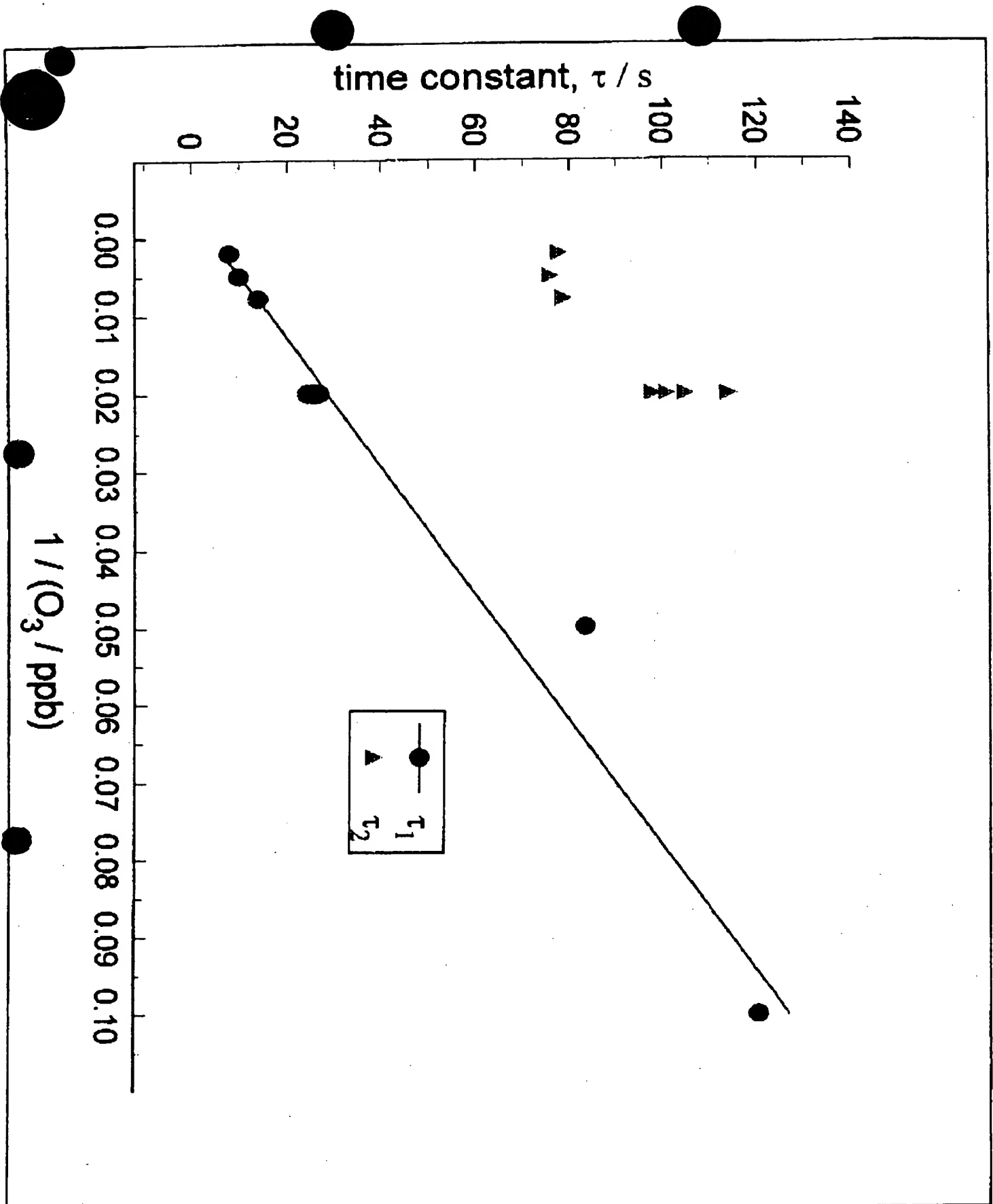


Fig. 2b

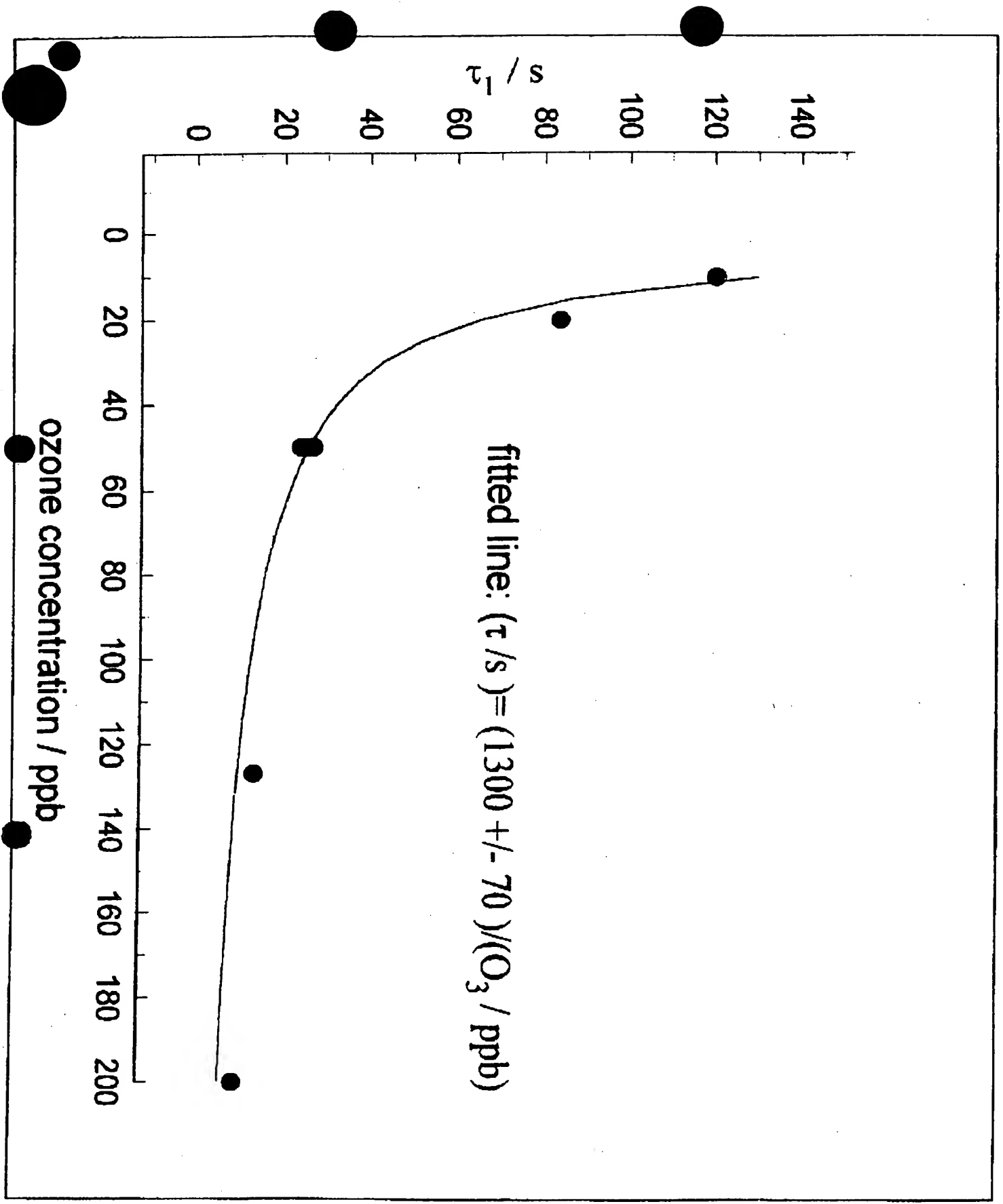


fig 2c

fitted model: $1/R = a + b/O_3$

parameters: $a = 1.81 \times 10^{-7} \Omega^{-1}$, $b = 2.55 \times 10^{-5} \Omega^{-1} \cdot \text{ppb}$

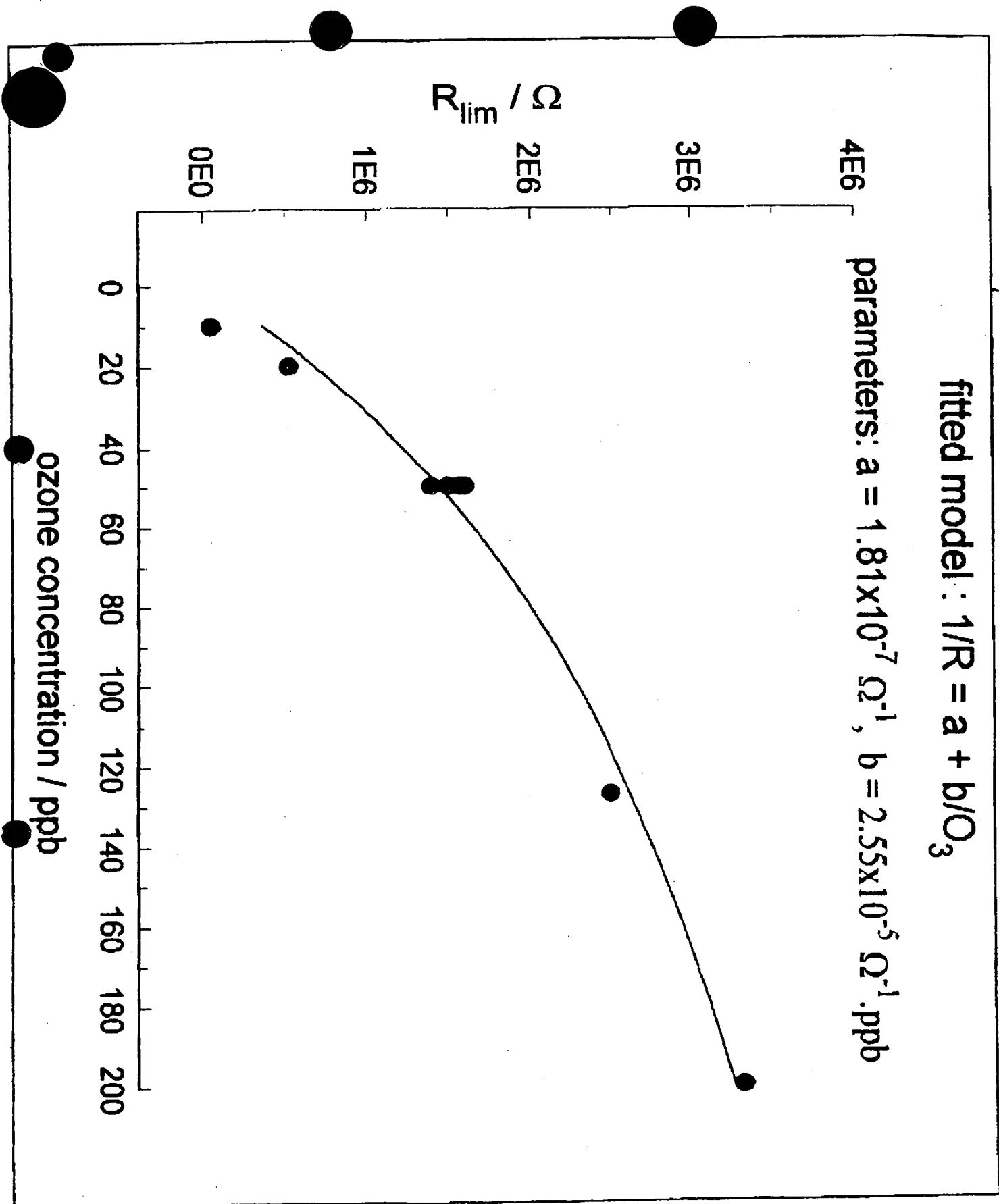
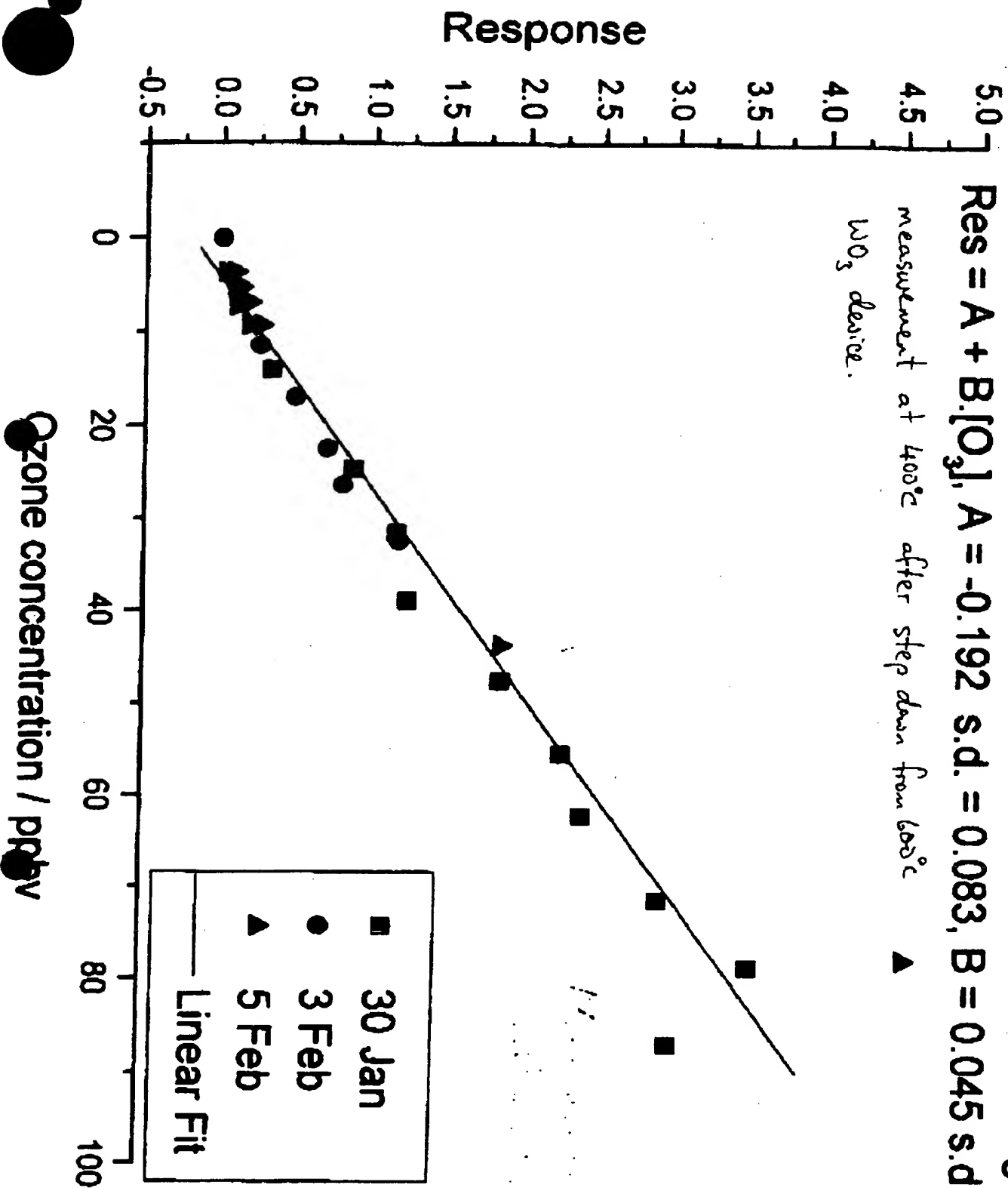


Figure 3

Graph showing Response at 128s against ozone concentration for all data with R. humidity = 49%. Data are fit with a straight line:

$$\text{Res} = A + B.[\text{O}_3], A = -0.192 \text{ s.d.} = 0.083, B = 0.045 \text{ s.d.} = 0.002.$$

measurement at 400°C after step down from 600°C
WO₃ device. ▲



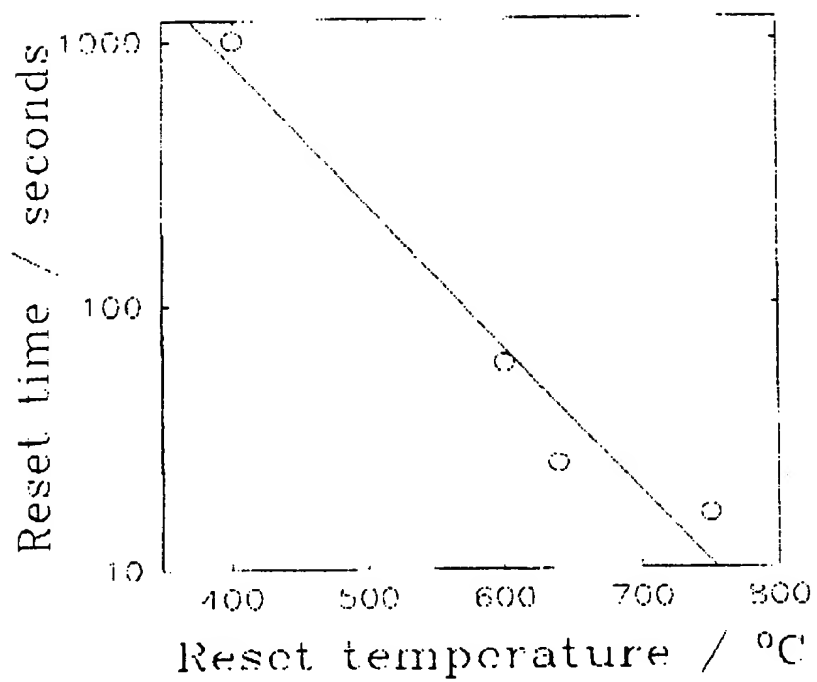


Figure 4. Time required at 'high' temperature to reset sensor surface before measurement at 'low' temperature.

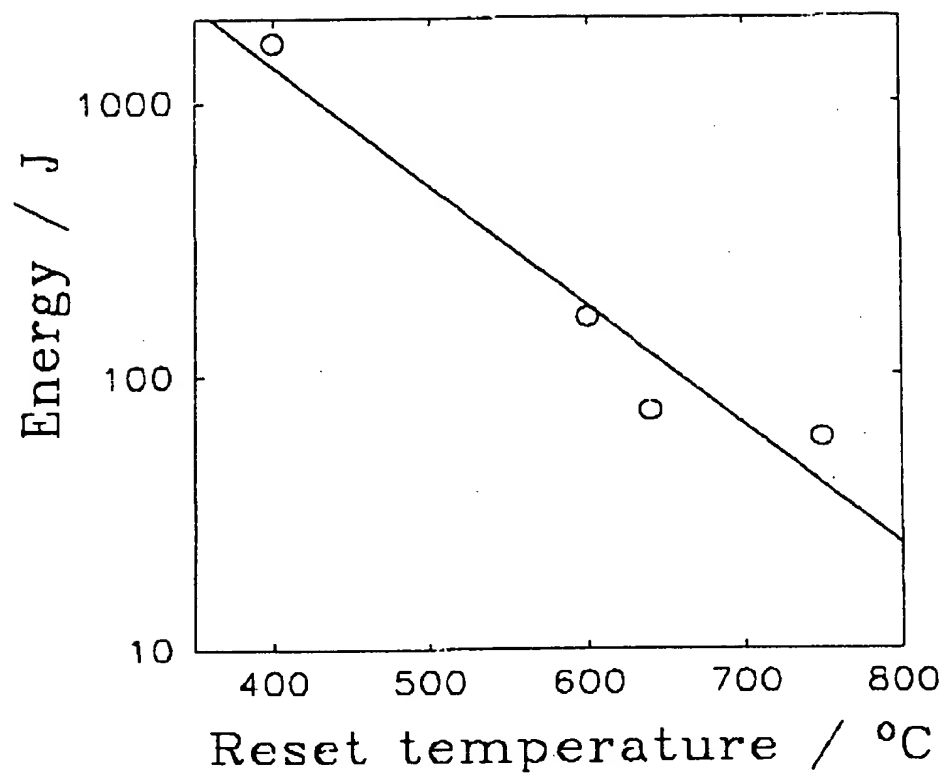


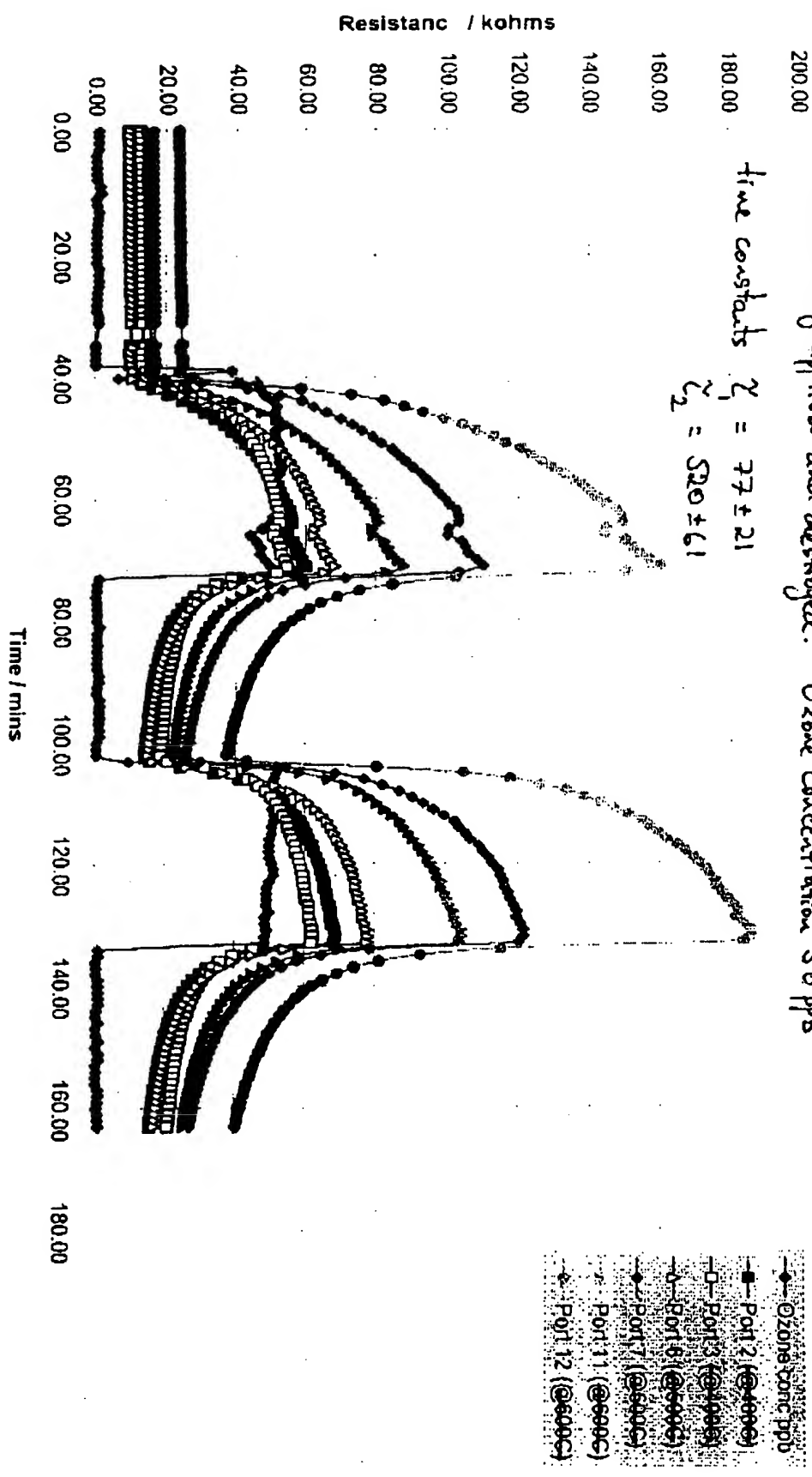
Figure 5 Energy consumption to reset the sensor surface, during the high temperature step.

Baseline stability: Sensors have been powered for 5 days (400, 580, and 600C) left unpowered for 30mins then a two cycle ozone test carried out at 500C. Filename expt1aozone.xls.

Date 17th August 1998.

Figure 6 Response of a number of 100 Ω sensors at constant temperature, 500C, when ozone is successively applied and destroyed. Ozone concentration 50 ppb

Time constants $\tau_1 = 77 \pm 21$
 $\tau_2 = 520 \pm 61$



keiths

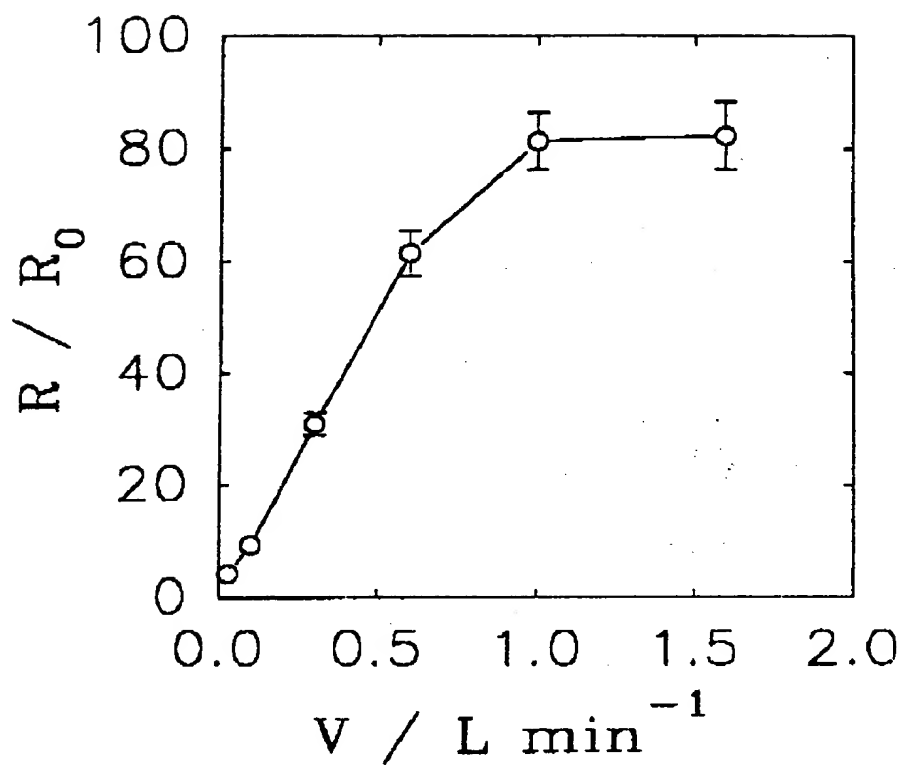


Figure 7 Effect of air flow rate on response of a WO_3 device at 400°C to 50ppb O_3 . 1L min^{-1}
 $\approx 20\text{ cm s}^{-1}$ flow velocity normal to the sensor